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(54) Title: HAIR COSMETIC COMPOSITIONS

(57) Abstract

A hair cosmetic composition comprising: (a) from about 0.01 % to about 3 % by weight of gelling agent comprising a copolymer of methyl vinyl ether/maleic anhydride, cross-linked with C₄-C₁₆ alkadiene or hydrolysis products thereof; (b) from about 0.1 % to about 10 % by weight of hair fixative polymer comprising a cationic copolymer of nonionic cellulose and diallyl dimethyl ammonium chloride; and (c) the balance comprising a carrier suitable for application to hair. The liquid hair cosmetic products have an improved non-tacky on-hair and on-hand feel, demonstrate excellent hair styling benefits in addition to ease of brush-out.

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HAIR COSMETIC COMPOSITIONS

Technical Field

The present invention relates to hair cosmetic compositions. More particularly, this invention relates to hair cosmetic compositions containing a gelling agent and a hair fixative/conditioning polymer and having improved "in-use" and "on-hair" feel properties in addition to manageability and style retention benefits.

Background Of The Invention

The desire to have the hair retain a particular shape is widely held. A common methodology for accomplishing this is applying hair styling, or "setting" compositions to the hair, typically to damp or dry hair. These compositions provide temporary setting benefits, and should be removable by water and/or by shampooing. The materials used in the compositions to provide the setting benefits are generally applied in the form of mousses, gels, lotions or sprays.

High levels of style retention, or hold, are typically expected from hair compositions whether applied as a gel or a spray. Style retention in gel products is typically achieved by use of one or more hair fixative

polymers, such as polyvinylpyrrolidone (PVP) and the copolymer of PVP with vinyl acetate (PVP/VA) in combination with a gelling agent. A commonly used gelling agent is crosslinked polyacrylic acid, known by the CTFA name of Carbomer. When such polymers are incorporated into hair fixative compositions containing conventional gelling agents they can provide suitable style retention attributes. However, such compositions can give a sticky feel on the hair and hands during and after application as well as leaving the hair feeling stiff and unnatural.

It has now been found that certain combinations of gelling agents and hair fixative polymers can deliver excellent styling benefits without the sticky and stiff feel usually associated with conventional styling gels.

Thus a need exists for hair styling compositions which deliver effective style retention, impart a hair conditioning effect, have a non-sticky hair and on-hand feel, are easily brushed out, are resistant to flakiness and at the same time have stable product and viscosity characteristics and remain fully stable under long term and stressed temperature storage.

Summary of the Invention

According to one aspect of the invention, there is provided a hair cosmetic composition comprising:-

- (a) from about 0.01% to about 3% by weight of gelling agent comprising a copolymer of methyl vinyl ether/maleic anhydride, crosslinked with C₄-C₁₆ alkadiene or hydrolysis products thereof;
- (b) from about 0.1% to about 10% by weight of hair fixative polymer comprising a cationic copolymer of nonionic cellulose and diallyl dimethyl ammonium chloride; and
- (c) the balance comprising a carrier suitable for application to hair.

The essential, as well as the optional, components of the present invention are described below. All levels and ratios are on a weight basis unless otherwise specified.

Gelling Agent

The compositions of the present invention contain from about 0.01% to about 3% preferably from about 0.05% to about 2%, more preferably from about 0.5% to about 1.5%, most preferably from about 0.6% to about 1% by weight of gelling agent. It is this gelling agent which in combination with a cationic hair fixative polymer imparts hair setting and conditioning benefits without the tacky dry-hair feel and on-hand stickiness normally associated with hair styling cosmetics. The gelling agents suitable for use in the present invention comprise a copolymer of methyl vinyl ether/maleic anhydride, and hydrolysis products thereof, crosslinked with C₄-C₁₆, preferably C₆-C₁₂, more preferably C₈-C₁₀ alkadiene. The gelling agents typically have a viscosity in the region of from about 50,000 cps to about 150,000 cps, preferably from about 70,000 cps to about 100,000 cps (measured as 0.5% gelling agent in non-alcoholic solution at pH7; Brookfield RVT, Spindle TE, 10 rpm).

In its broadest aspect, the copolymer utilised in the present application comprise a copolymer of methyl vinyl ether/maleic anhydride (hereafter identified as A) crosslinked with C₄-C₁₆, preferably C₆-C₁₂, more preferably C₈-C₁₀ alkadiene (hereafter identified as B). Examples of suitable polymers and their preparations are described in detail in "Polymers and Thickeners" Vol. 108, May 1993, p61-67, S.L. Kopolow, Y.T. Kwak and M.Helioff. These polymers comprise part A and B as defined above. In preferred embodiments, B comprises C₆-C₁₄ alkadiene, more preferably a C₆-C₁₂ alkadiene, most preferably a C₈-C₁₀ alkadiene.

The preferred gelling agent for use herein is methyl vinyl ether/maleic anhydride, crosslinked with 1,9-decadiene (PVM/MA decadiene crosspolymer), available from ISP as Stabileze 06 (RTM).

The hair gelling agents, herein are preferably utilised in at least partially neutralised form in order to obtain the required gel structure and overall pH of the hair cosmetic compositions.

The gelling agent can be neutralised to a level of from about 30% to about 100%, preferably from about 40% to about 98%, more preferably from about 50% to about 95% with base. Any conventionally used base, organic or inorganic, may be used for neutralisation of the acidic gelling agents. Hydroxides of alkali and alkaline earth metals and amino alcohols are suitable neutralisers for use in the present hair cosmetic compositions.

Examples of suitable organic neutralising agents which may be included in the hair cosmetic compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amine-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA), dimethyl steramine (DMS) and amino methyl propanol (AMP) and mixtures thereof.

Preferred neutralising agents for use in compositions of the present invention are potassium and sodium hydroxides, aminomethyl propanol (AMP) and triethanolamine (TEA) and mixtures thereof.

In addition to the specific gelling agents as detailed *supra* such compositions may optionally include an auxiliary gelling agent at from about 0.01% to about 1%, preferably from about 0.1% to about 0.5% by weight. Suitable auxiliary gelling agents can be selected from any conventional gelling agent such as a crosslinked polyacrylic acid copolymer, ethylene maleic anhydride copolymers or hydroxyethylcellulose and its derivatives. The preferred auxiliary gelling for use herein is hydroxyethylcellulose.

Carrier

The hair cosmetic compositions of the present invention also include a carrier which can be aqueous or non-aqueous and mixtures thereof. This can comprise any of those conventionally used in polymer containing hair cosmetic formulations. The carrier is generally present in the hair cosmetic compositions at from about 70% to about 99.89%, preferably from about 78% to about 99.5% by weight. More preferably, the carrier is present at from about 80% to about 99% by weight of the total composition.

Organic solvents suitable for use in the carrier in compositions according to the present invention include C₁-C₆ alkanols, carbitol, acetone and mixtures thereof. C₁-C₆ alkanols preferred for use in the present compositions are C₂-C₄ monohydric alcohols such as ethanol, isopropanol and mixtures thereof.

The preferred hair compositions according to the present invention contain from 70% to about 99.89% by weight of water, preferably from 78% to about 99.5%, more preferably from about 80% to about 99% by weight of water as the carrier.

Cationic Hair Fixative Polymer

In addition to the gelling agent the compositions according to the present invention comprise, as a second essential component, a hair fixative polymer. This hair fixative polymer is preferably solubilized or colloidally dispersed in the hair cosmetic carrier along with the gelling agent copolymer.

The preferred hair fixative polymer component of the hair cosmetic compositions of the present invention comprises a cationic copolymer of hydroxyethyl cellulose and diallyl dimethyl ammonium chloride which is known by the CTFA name Polyquaternium 4 and marketed under the trade names Celquat L200 (RTM) and Celquat H100 (RTM) by National Starch and Chemical Ltd.

The hair fixative polymer is present in an amount of from about 0.1% to about 10%, preferably from about 0.3% to about 8%, more preferably from about 0.5% to about 6%, most preferably from about 0.8% to about 3% by weight of composition. In compositions according to the present invention the weight ratio of gelling agent:hair fixative polymer is in the range of from about 10:1 to about 1:10.

Other hair fixative polymers suitable for use herein in conjunction with the above material include any polymer which is soluble or colloiddally dispersible in the hair cosmetic carrier. Solubility and dispersibility are determined at ambient conditions of temperature and pressure (25°C and at 101.3 kPa (1 Atm)). Such copolymers may be cationic or nonionic in character. Copolymers suitable for use herein have a molecular weight in the range of from about 1,000 to about 5,000,000, preferably from about 50,000 to about 4,000,000, more preferably from about 100,000 to about 3,000,000, most preferably from about 500,000 to about 2,000,000.

In addition cationic and nonionic resins may be utilised as detailed below. Polycationic hair conditioning polymer resins suitable for use herein are described below. For convenience in describing the polymers hereof, monomeric units present in the polymers may be referred to as the monomers from which they can be derived. The cationic monomers can be derived from polymerizable cationic starting monomers, or from polymerizable nonionic monomers which are modified subsequent to polymerization to be of cationic character.

These cationic unsaturated monomers can be polymerized in cationic form, or as an alternative they can be polymerized in the form of their precursors, which are then modified to be cationic, for example, by a quaternizing agent (eg. ethyl monochloroacetate, diethyl sulfate, etc.). Preferred cationic monomers include dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, diallyldimethyl ammonium chloride, vinylimidazolium quaternary ammonium monomers and mixtures thereof.

Representative examples of nonionic monomers are acrylic or methacrylic acid esters of C1-C24 alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-

pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-24 preferably from about 4-18, more preferably from about 4-12 carbon atoms; styrene; chlorostyrene; vinyl esters such as vinyl acetate; vinyl chloride; vinylidene chloride; acrylonitrile; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; alkoxyalkyl (meth)acrylate, such as methoxy ethyl (meth)acrylate and butoxyethyl (meth)acrylate; and mixtures thereof. Other nonionic monomers include acrylate and methacrylate derivatives such as allyl acrylate and methacrylate, cyclohexyl acrylate and methacrylate, oleyl acrylate and methacrylate, benzyl acrylate and methacrylate, tetrahydrofurfuryl acrylate and methacrylate, ethylene glycol di-acrylate and -methacrylate, 1,3-butyleneglycol di-acrylate and -methacrylate, diacetoneacrylamide, isobornyl (meth)acrylate, and the like.

Preferred nonionic monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

Representative polar nonionic monomers include acrylamide, N,N-dimethylacrylamide, methacrylamide, N-t-butyl acrylamide, methacrylonitrile, acrylamide, acrylate alcohols (eg. C2-C6 acrylate alcohols such as hydroxyethyl acrylate, hydroxypropyl acrylate), hydroxyethyl methacrylate, hydroxypropyl methacrylate, vinyl pyrrolidone, vinyl ethers, such as methyl vinyl ether, acyl lactones and vinyl pyridine, allyl alcohols, vinyl alcohols and vinyl caprolactam.

Preferred polycationic polymer resins for use herein include cationic guar gum, cationic polysaccharides, homopolymers of dimethyldiallyl ammonium chloride, copolymers of dimethyldiallyl ammonium chloride and acrylamide, cationic amino-functional homopolymers and copolymers derived from acrylic acid and/or methacrylic acid, especially from alkylaminoalkyl acrylate and methacrylate monomers such as

dimethylacmonoethyl acrylate and methacrylate, polyalkylene imines and ethoxy polyalkylene imines, vinylimidazolium/vinylpyrrolidone quaternary ammonium copolymers, and mixtures thereof.

The auxilliary hair fixative polymer is incorporated with the Polyquaternium 4 at levels of from about 0.01% to about 10%, preferably from about 0.15 to about 5% by weight. The combination of Polyquat 4 and auxilliary hair fixative polymer is valuable for providing overall hair feel benefits, particularly with respect to flakiness.

The present compositions can be formulated as leave-in hair cosmetic compositions such as gels or creams. Methods of making the hair cosmetic compositions of the present invention are described more specifically in the examples.

The hair cosmetic compositions of the present invention may contain a chelating agent at a level of from about 0.01% to about 5%, preferably from about 0.5% to about 3%, more preferably from about 0.08% to about 1% by weight. Chelating agents suitable for the compositions according to the present invention include salts of ethylenediamine tetraacetic acid including ethylenediamine tetraacetic acid, disodium ethylenediamine tetraacetic acid and pentasodium pentatate. The preferred chelating agent for use in compositions according to the present invention is tetrasodium ethylenediamine tetraacetic acid.

The hair cosmetic compositions of the present invention can also contain a variety of non-essential, optional components such as preservatives, surfactants, block polymers, thickeners and viscosity modifiers, electrolytes, fatty alcohols, pH adjusting agents, perfume oils; UV screening agents; hair conditioning agents, Pearlescents, emollients; lubricants and penetrants such as various lanolin components; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; volatile and non-volatile silicone fluids. Such conventional optional ingredients are well known to a person skilled in the art, e.g. surfactants used as perfume solubilizing agents such as anionics (e.g., sodium alkyl sulphates, nonionics (amine oxides);

amphoterics (aliphatic secondary or tertiary amine derivatives) zwitterionics (aliphatic quaternary ammonium; phosphonium or sulphonium derivatives) and fluorinated surfactants (e.g. Zonyl FSK) (RTM), preferred surfactants for use herein being nonionics such as polyethylene glycol fatty acid esters, isosteareth-20, polysorbate-20, PPG-12-PEG-65 lanolin oil, PEG-40 hydrogenated castor oil, polysorbate 80, Oleth-20 and Nonoxynol-10, thickeners and viscosity modifiers such as diethanolamides of long chain fatty acids, sodium chloride, sodium sulphate, and ethyl alcohol; block polymers of ethylene oxide and propylene oxide such as Pluronic (RTM) F88 offered by BASF Wyandotte; preservatives such as DMDM hydantoin, methyl paraben, propyl paraben and diaxolidinyl urea; fatty alcohols such as cetearyl alcohol; electrolyte such as earth and alkaline-earth metal salts; quaternary ammonium ions and cationic amines and halogen ions; pH adjusting agents such as citric acid, succinic acid, sodium hydroxide and triethanolamine; perfume oils such as Florasynth (RTM) perfumes; hair conditioning agents such as panthenol/pantyl B and pearlescing agents such as ethylene glycol distearate and mica and UV screening agents such as benzophenone-4 and benzophenone-10. Each of these optional materials can be present at a level of from about 0.01% to about 5%, preferably from about 0.05% to about 3%, most preferably from about 0.08% to about 1%, by weight of composition.

The hair cosmetic compositions of the present invention are used in conventional ways to provide the hair styling/holding benefits of the present invention in combination with reduced on-hair and on-hand tack. Such methods can involve applying an effective amount of the product to dry or damp hair before or after the hair is styled, or both. By "effective amount" is meant an amount sufficient to provide the hair volume and style benefits desired considering the length and texture of the hair. The hair cosmetic compositions according to the present invention may be effectively applied to the hair using the hands, using a comb or brush or by applying with a sponge or 'wipe'.

The invention is illustrated by the following non-limiting examples.

Gelling agent	-	Stablileze 06 (RTM)
Neutralising agent	-	Triethanolamine (TEA)
Hair fixative polymer A	-	Polyquaternium 4 (RTM)
Hair fixative polymer B	-	PVP/VA
Chelating agent	-	tetra sodium ethylenediamine tetracetic acid EDTA (Na) ₄

Examples	I	II	III
Stablileze 06	0.6	0.4	0.3
Carbomer 980/201	-	0.2	
TEA	0.6	0.6	0.3
Polyquat 4	1.0	0.5	1.0
PVP/VA	-	0.5	0.5
EDTA (Na) ₄	0.1	0.1	0.1
Ethanol	-	-	10.0
Water	To balance	To balance	To balance

The hair cosmetic formulations are prepared by (a) dispersing the gelling agent(s) into water, allowing sufficient time for hydration of the gelling agent (30 minutes to 1 hour), then partially neutralising the gelling agent with a suitable base and (b) in a separate step, solubilising the fixative polymer(s) in water along with any non-essential optional ingredients and the chelating agent. The premixes (a) and (b) are combined and the resulting mixture is modified to the desired viscosity and pH characteristics using the remainder of the neutralising base.

The above compositions provide effective style retention, deliver a hair conditioning effect with low on-hand and on-hair tack.

CLAIMS

1. A hair cosmetic composition comprising:-
 - (a) from about 0.01% to about 3% by weight of gelling agent comprising a copolymer of methyl vinyl ether/maleic anhydride, crosslinked with C₄-C₁₆ alkadiene or hydrolysis products thereof;
 - (b) from about 0.1% to about 10% by weight of hair fixative polymer comprising a cationic copolymer of nonionic cellulose and diallyl dimethyl ammonium chloride; and
 - (c) the balance comprising a carrier suitable for application to hair.
2. A hair cosmetic composition according to Claim 1 wherein the viscosity of the gelling agent at 25°C is in the region of from about 70,000 cps to about 100,000 cps (measured as 0.5% gelling agent in non-alcoholic solution at pH7; Brookfield RVT, Spindle TE, 10rpm).
3. A hair cosmetic composition according to Claims 1 or 2 wherein the level of gelling agent is from 0.05% to about 2%, preferably from about 0.5% to about 1.5%, more preferably from about 0.6% to about 1.0% by weight.
4. A hair cosmetic composition according to any of Claims 1 to 3 wherein the gelling agent is neutralized to a level of from about 30% to about 95%, preferably from about 40% to about 80%, more preferably from about 50% to about 60% with base.
5. A hair cosmetic composition according to Claim 4 wherein the base is selected from alkali metal, alkaline earth metal and ammonium hydroxides, amines and amino alcohols and mixtures thereof and in particular is selected from triethanolamine, sodium hydroxide and mixtures thereof.

6. A hair cosmetic composition according to any of Claims 1 to 5 wherein the weight average molecular weight of the cationic copolymer is in the range of from about 1,000 to about 5,000,000.
7. A hair cosmetic composition according to any of Claims 1 to 6 wherein the cationic copolymer comprises a copolymer of hydroxy ethyl cellulose and diallyldimethyl ammonium chloride.
8. A hair cosmetic composition according to any of Claims 1 to 7 wherein the hair fixative polymer is present at a level of from about 0.5% to about 8%, preferably from about 0.8% to about 6%, more preferably from about 1% to about 3% by weight.
9. A hair cosmetic composition according to any of Claims 1 to 8 wherein the weight ratio of gelling agent: hair fixative polymer(s) is in the range of from about 10:1 to about 1:10.
10. A hair cosmetic composition according to any of Claims 1 to 9 wherein the carrier system comprises water and optionally organic solvent selected from C₁-C₆ alkanols, diols, polyols, carbitols, acetone and mixtures thereof.
11. A hair cosmetic composition according to any of Claims 1 to 10 wherein the gelling agent copolymer crosslinking agent is an alkadiene selected from C₄-C₁₆ alkadienes, preferably C₆-C₁₄ alkadienes, more preferably C₆-C₁₂ alkadienes, most preferably a C₈-C₁₀ alkadiene such as 1,9-decadiene.
12. A hair cosmetic composition according to any of Claims 1 to 11 wherein the gelling agent is a copolymer of methyl vinyl ether/maleic anhydride crosslinked with 1,9-decadiene.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US95/08336

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A61K 7/06

US CL : 424/70.11, 70.17

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : A61K 7/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,194,260 (GROLIER ET AL.) 16 MARCH 1993, column 8,9 and 16.	1-3
Y	US, A, 5,118,498 (HELIOFF ET AL.) 02 JUNE 1992, column 1-4.	1-3
Y	US, A, 5,066,481 (HELIOFF ET AL.) 19 NOVEMBER 1991, column 1-4.	1-3

☐

Further documents are listed in the continuation of Box C.

☐

See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

29 AUGUST 1995

Date of mailing of the international search report

17 OCT 1995

Name and mailing address of the ISA/US
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/08336

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-12
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐
☐

- The additional search fees were accompanied by the applicant's protest.
No protest accompanied the payment of additional search fees.